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(54) Title: GOLD CATALYST FOR FUEL CELLS

(57) Abstract

Gold catalyst for reforming and electrochemical oxidation of hydrocarbon fuels, methanol and methane, for application in the fuel cell industry. The gold catalyst is suitable for removal of impurities from the anodic fuel, by selective oxidation of the carbon monoxide. The active component of the catalyst is a complex which consists of gold and reducible oxide from the transition metals group. The concentration of the gold is from 0.1 % to 2.5 % and the concentration of the transition metal is from 0.1 % to 5 %. The support of the catalyst consists of oxides of ceria, zirconia and titanium. The working temperature of the catalyst is from ambient to 650 °C.

GOLD CATALYST FOR FUEL CELLS

Background of the invention

The invention relates to a gold catalyst for oxidation of hydrocarbon and thus suitable for the fuel cell industry.

Fuel cells are attractive alternative to the internal combustion engine technology, since they offer zero emission, higher efficiency and reliability.

The commercialisation of the fuel cells however, has been delayed due to technical and economic considerations, which include the availability of a suitable fuel in sufficient quantity and at competitive price and the lack of catalyst for the anodic reaction active at low temperatures. One of the best fuels is hydrogen, but its production is a power hungry and costly.

During the last two decades of the modern development of fuel cells, several fuels other than hydrogen were considered; hydrocarbons, methanol, hydrazine and ammonia. Of this hydrazine has shown to be carcinogenic, and ammonia to be expensive. Hydrocarbons, natural gas and methanol therefore, could be the fuels of choice as they are cheap and available in large quantity.

The direct methanol fuel cell (DMFC) has been considerate as the ideal fuel cell system since it produces electric power by the direct conversion of methanol at the fuel cell anode. The DMFC is more attractive than the conventional hydrogen fuel cells especially for transportation, where at present bulky gas bottles with compressed hydrogen are carried. However, commercialisation of DMFC has been impeded, major limitation being the

anode performance which requires highly efficient and cost effective oxidation catalyst which at present is still not available.

Catalysts of prior art

Where base metal are used, degradation of the catalyst rapidly occurs. Platinum group metals have been used to some advantages, but sufficiently high activity at low metal loading has not been achieved. Further platinum is active at temperatures higher than 200°C and moisture has a negative effect at low working temperatures. Fuel cells have also been operated at high temperature to compensate for the low catalyst activity. This exacerbates catalyst degradation and raises the overall termal signature of the device.

Gold has always been regarded as far less active than the platinum group methals (PGM's). Recent publications, however, have shown that gold, when highly dispersed on reducible oxides, is very active for carbon monoxide oxidation at low temperature.

For example, German patent DE 3914294 describes a gold catalyst dispersed on a support containing iron oxide and alumine oxide and/or aluminosilicate. This catalyst, however, has unsatisfactory conversion of carbon monoxide at higher space velocity and is poisoned by moisture and sulphur dioxide.

Bulgarian patent No. 101,490 describes gold catalyst for oxidation of carbon monoxide and hydrocarbons, reduction of nitrogen oxides and decomposition of ozone. The catalyst is suitable for removing toxic exhaust gases from the combustion engine, for decomposition of ozone at low temperatures, etc.

Summary of the invention

Clearly, more active catalyst with high efficiency, acceptable cost and low operating temperature is required.

According to the invention, a catalyst for direct electrochemical oxidation of methanol, hydrocarbons and methane comprises a complex of gold and reducible oxide of a transition metal on a porous support of oxides selected from ceria, titanium and zirconia.

The transition metal could be chromium, copper, cobalt, manganese, iron or a combination of those metals. The concentration of the gold is from 0.1 % to 2.5%, but preferably less than 1.3% and the total concentration of the metals in the active composition should not exceed 6% from the total mass of the catalyst.

The support of mixed oxides has large surface area typically 80 m²/g to 400 m²/g, with ceria oxide concentration from 30% to 70 %, titania oxide 5% to 25% and zirconia oxide from 5% to 25%.

The gold-transition metal oxide particles are deposited on the support by the methods of the known art: impregnation, precipitation, co-precipitation, wet incipient dryness or a combination of these techniques. The particles of the active component are finely and evenly dispersed through the support and should be of a size less than 40 nm, preferably less than 20 nm.

The calcination of the catalyst is maintained in oxidising atmosphere at temperature from 100° to 500°C. The working temperature of the catalyst is from 0 o to 650°C.

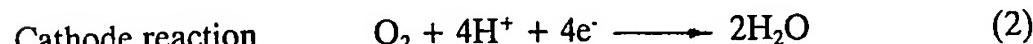
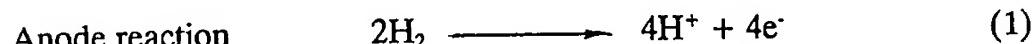
The catalyst could have applications in the following areas of the fuel cell technology:

- Direct electrochemical oxidation of methanol
- Reforming of methane
- Direct electrochemical oxidation of liquid fuels at temperatures lower than what is currently used.
- Removal of impurities, mainly carbon monoxide, from the anodic fuel.

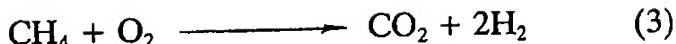
Fuel cells are electrochemical energy converters. They consist of two electrodes containing electrocatalysts and an electrolyte. Gas fuel is fed to the anode and is absorbed on the catalitically active surface, where an oxidation reaction occurs.

After the electrons are discharged, the ionized fuel passes through the electrolyte and on the surface of the cathode absorbs electrons and combines with oxygen thus forming water. This process could take place at temperature below 100°C.

The reactions taking place on the anode and the cathode are:



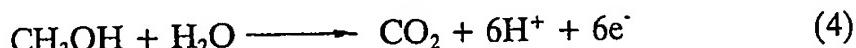
The force behind the process of ion migration is the concentration gradient between the two interfaces, electrode and electrolyte. The oxidation of methane could generate hydrogen, required for the electrochemical oxidation at the anode of the fuel cell:



The research today has shown however, that this can not be achieved with the existing commercial catalysts. Even with noble metals, the best reported to be Pt supported on carbon, the conversion has proven insufficient.

The direct methanol fuel cell (DMFC) has been considered as the ideal fuel cell since it provides electric power by the direct conversion of methanol at the fuel cell anode. The DMFC is more attractive than conventional hydrogen fuelled cells particularly for transportation applications.

The conversion of methanol takes place according to the following reaction:



Commercialisation of the direct methanol fuel cell however, has been impeded by its poor performance compared with hydrogen-air systems, the major limitation being the anode performance for which highly efficient methanol oxidation catalysts are required.

The advantages of the catalyst of the invention

- The gold catalyst may be used for direct electrochemical oxidation and of hydrocarbons at low temperatures, below their thermal decomposition.
- The catalyst of the invention oxidises methanol at temperature below 100°C.
- The catalyst could be suitable for direct conversion of methane.
- The gold catalyst is highly efficient oxidation catalyst: total oxidation of methane to carbon dioxide occurs even under partial oxidation conditions.

- The complete oxidation of methane occurs below 550°C.
- The presence of moisture enhances the catalyst's oxidation activity, and thus makes it very attractive for steam reforming.
- The loading of the gold in the catalyst is at acceptable low levels which makes the catalyst economically viable.
- The exceptionally high oxidising capacity of the catalyst of the invention at low temperature, could be utilised for the removal of impurities, from the anodic fuel by selective oxidation of carbon monoxide.

Description of examples

Six samples of the catalyst of the invention were tested for oxidation of methane. The samples vary in their gold content and composition of the support.

The catalyst were tested in reaction gas mixture containing 0.25% CH₄ balance air and 2.5% CH₄, balance air at a gas hourly space velocity (GHSV) of 12 000 h⁻¹.

Example 1

Tests in a 0.25% methane , balance air

Samples 1, 2, 3 were tested in the gas mixture at temperature from ambient up to 500°C. The temperature range for samples 4, 5, 6 was increased to 600°C.

The space velocity was 12 000 h⁻¹.

After testing to the maximum temperature, the samples were cooled in air to room temperature and re-tested in the same reaction mixture, to evaluate catalyst stability and reproducibility.

The total methane conversion, as a function of reaction temperature, has been determined for each catalyst and the results are given in Figure 1. Run 2 in the same figure denote the repeat test.

From Figure 1, it can be seen that the methane conversion occurs between 400 and 550°C. The best catalytic activity is achieved by sample 6.

The repeat run showed that the catalysts are stable at temperatures as high as 600°C under the test conditions. Further, operating at high temperatures, primed catalyst number 6 and improved its performance.

Example 2

Tests in a 2.5% methane, balance air

The same samples 1, 2, 3, 4, 5 and 6 were tested in 2.5% methane, balance air to a temperature of 600°C, and GHSV = 12 000 h⁻¹.

To evaluate catalyst stability and reproducibility, sample 6 was cooled in air from 600°C to room temperature and re-tested in the gas mixture again to 600°C.

From the results shown in Figure 2 it can be seen that increasing the concentration of methane by a factor of 10 (i.e.: from 0.25% to 2.5%) does not alter significantly the conversion of methane. Again catalyst 6 showed excellent activity for methane oxidation and stability up to 600°C. (Figure 2, Run 2.)

Example 3**Tests in 25% methane, balance air**

Sample 4 was tested for partial oxidation of methane in the following gas mixtures:

- (a) 25% CH₄, 15.8% O₂, balance N₂
- (b) 25% CH₄, 3.9% O₂, balance N₂

The total methane conversion and selectivity of products to CO₂ and CO was determined as a function of temperature.

For each experiment the catalyst activity was evaluated up to 600°C.

After testing to 600°C, the catalyst was cooled in air to room temperature and the reaction repeated in order to establish catalyst stability and reproducibility. The results in test mixture (a) are given in Figure 3 and the results in test mixture (b) are given in Figure 4. In both figures the repeat test are shown in Run 2.

From Figures 3 and 4, it can be seen that the gold catalyst showed almost complete product selectivity to the formation of carbon dioxide even when the oxygen content was reduced and the O₂/CH₄ ratio was changed from 1 : 1.06 to 1 : 6.4. Thus, when reaction condition were most favourable for partial oxidation, the catalyst showed excellent total oxidation properties.

Example 4

Tests for methanol oxidation were carried out with samples 2 and 5. The experiments were performed by pumping liquid methanol into a vaporiser. The gas mixture was 6.5% CH₃OH, balance air and gas hourly space velocity 20 000 h⁻¹. The results are given in Table 1 and show that Sample 5, which contains higher concentration of gold and titanium oxide, is superior in respect to the methanol oxidation.

Table 1

Temperature (°C)	CH ₃ OH oxidation %	
	Sample 2	Sample 5
50	20	100
100	69	100

Example 5

Comparison between the gold catalyst of the invention and platinum catalyst on aluminium oxide support was carried out. The Pt loading was six times higher than the gold content. The gas mixture used in the experiment was 10.5% CH₃OH, balance air, gas hourly space velocity 60 000h⁻¹.

Irrespective of its lower metal loading (six times less), the gold catalyst shows significantly better oxidation activity at temperatures below 100°C.

Table 2

Temperature (°C)	CH ₃ OH oxidation %	
	Au catalyst	Pt catalyst
30	99	50
50	100	80
100	100	99

Example 6

In addition to its high activity for oxidation of methanol and hydrocarbons, the gold catalyst of the invention shows exceptional capacity for oxidation of carbon monoxide at ambient temperature. This could be utilised for the removal of impurities, mainly CO, from the anodic fuel. Comparison between the gold catalyst and platinum catalyst shows the superiority of the catalyst of the invention. The test was carried with a gas mixture containing 1% CO, balance air at gas hourly space velocity 60 000h⁻¹.

Table 3

Temperature (°C)	CO oxidation %	
	Au catalyst	Pt catalyst
25	100	2
100	100	12

PATENT CLAIMS

1. A gold catalyst for direct electrochemical oxidation of hydrocarbon fuels at temperature lower enough to avoid thermal cracking of the fuel, including active complex and support, where the catalyst contains gold-reducible oxide clusters on a support consisting of oxides of ceria, zirconia and titanium, the concentration of the metals in the active complex is from 0.1% to 6%, the total mass of gold being from 0.1% to 2.5%, but preferably less than 1.3%.
2. A gold catalyst according to claim 1, where the reducible oxide can be one or more oxides of copper, chromium, cobalt, iron and manganese.
3. A gold catalyst according to claim 1, where the concentration of the reducible oxide in the active cluster is between 0.1% and 5%.
4. A gold catalyst according to claim 1, where the support of the catalyst consists of oxides of ceria, zirconia and titanium or a mixture of these.
5. A gold catalyst according to the above claims, where the concentration of the ceria oxide could be from 30% to 70%, the titanium oxide from 5% to 25% and the zirconia oxide from 5% to 25%.
6. Use of gold catalyst for oxidation of hydrocarbon fuels, methanol, methane and carbon monoxide at working temperatures from 0° to 650°C.
7. Use of gold catalyst according to claim 6, which is suitable for the reforming of methane.

8. Use of gold catalyst according to claim 6, for direct electrochemical oxidation of methanol.
9. Use of gold catalyst according to claim 6, suitable for selective oxidation of carbon monoxide impurities from the anodic fuel.

Figure 1:
Total Methane Oxidation (0.25% CH₄, 20% O₂)

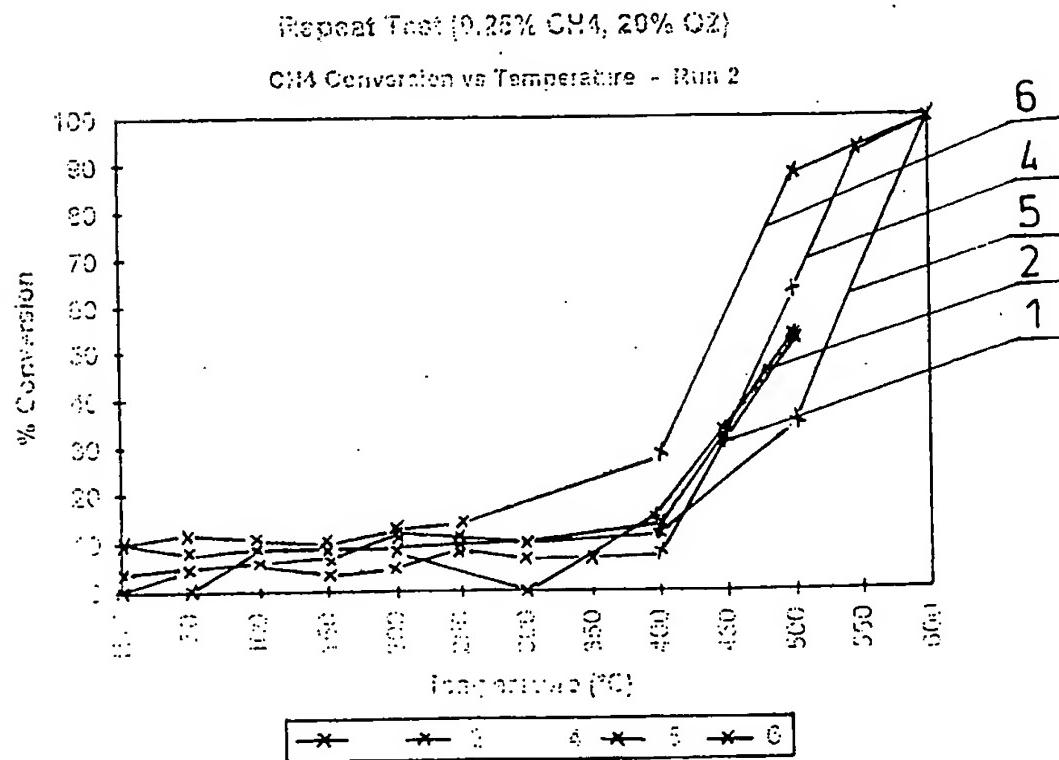
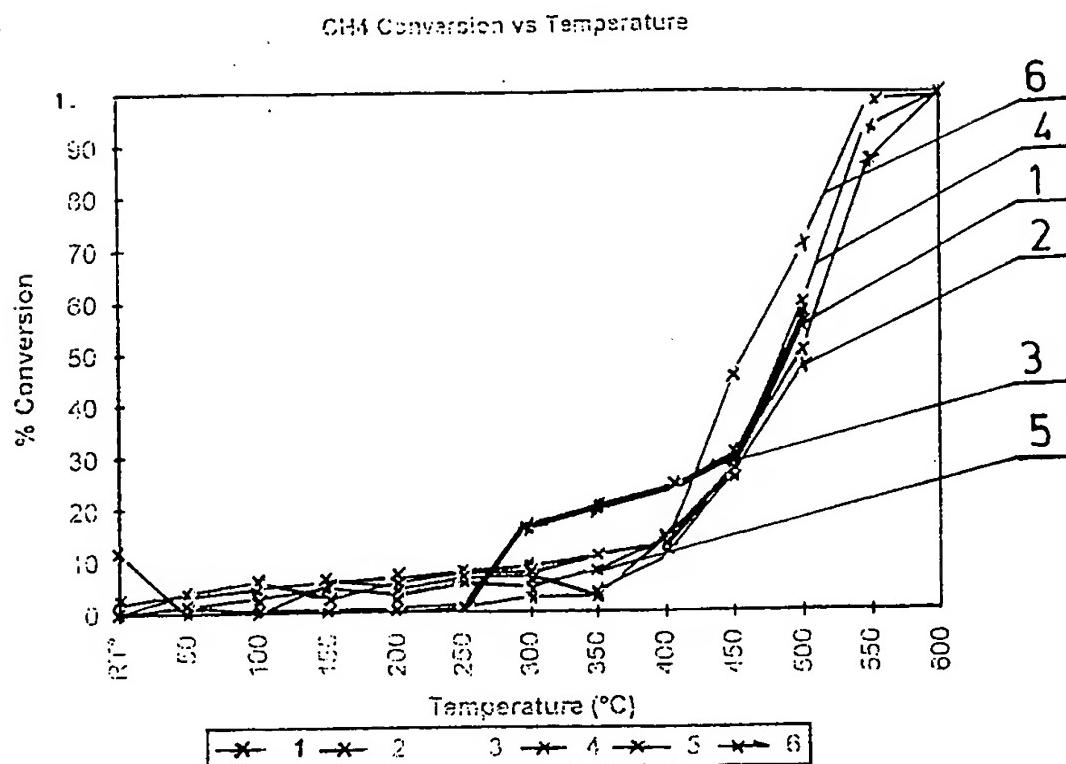
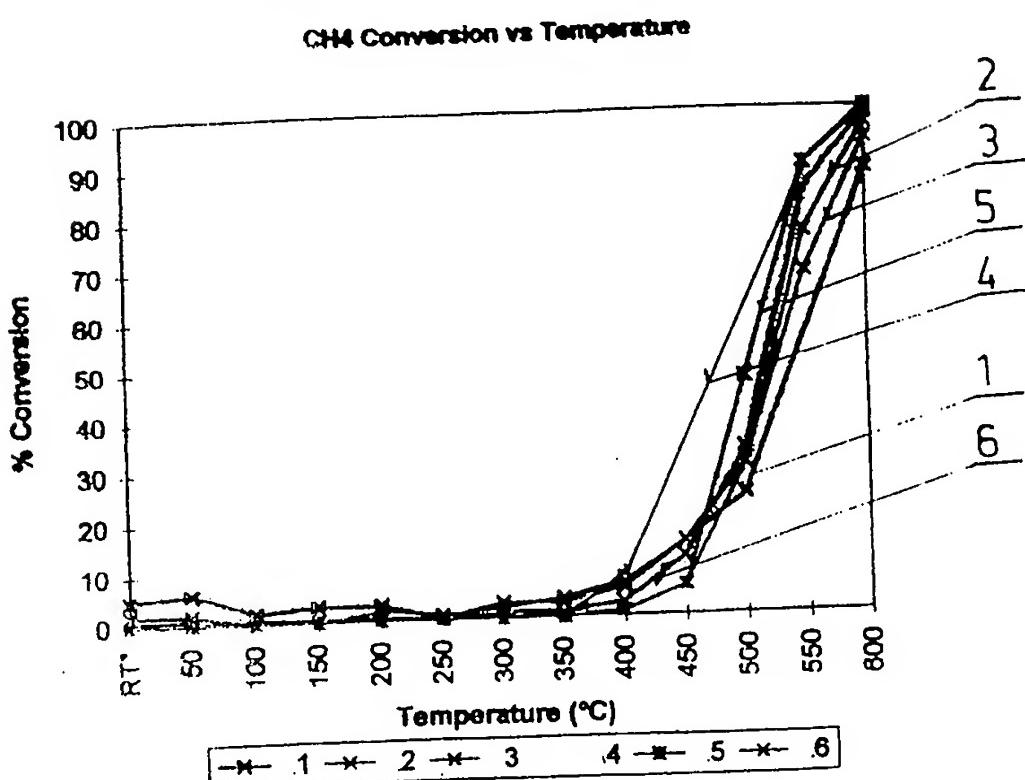
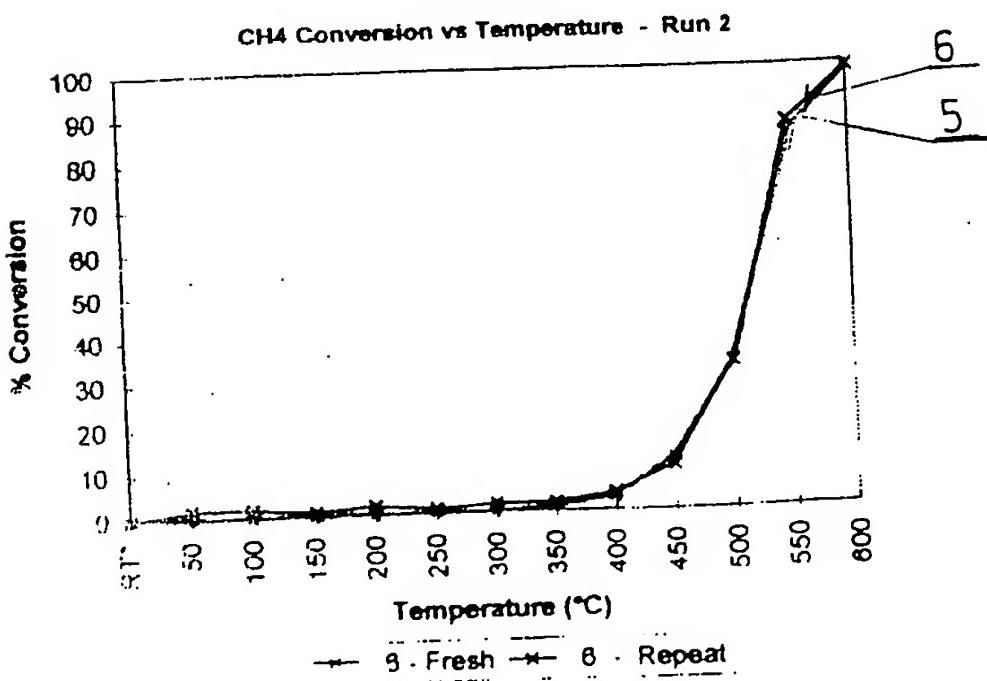


Figure 2:
Total Methane Oxidation (2.5% CH₄, 20% O₂)



Repeat Test (2.5% CH₄, 20% O₂)
Sample 6



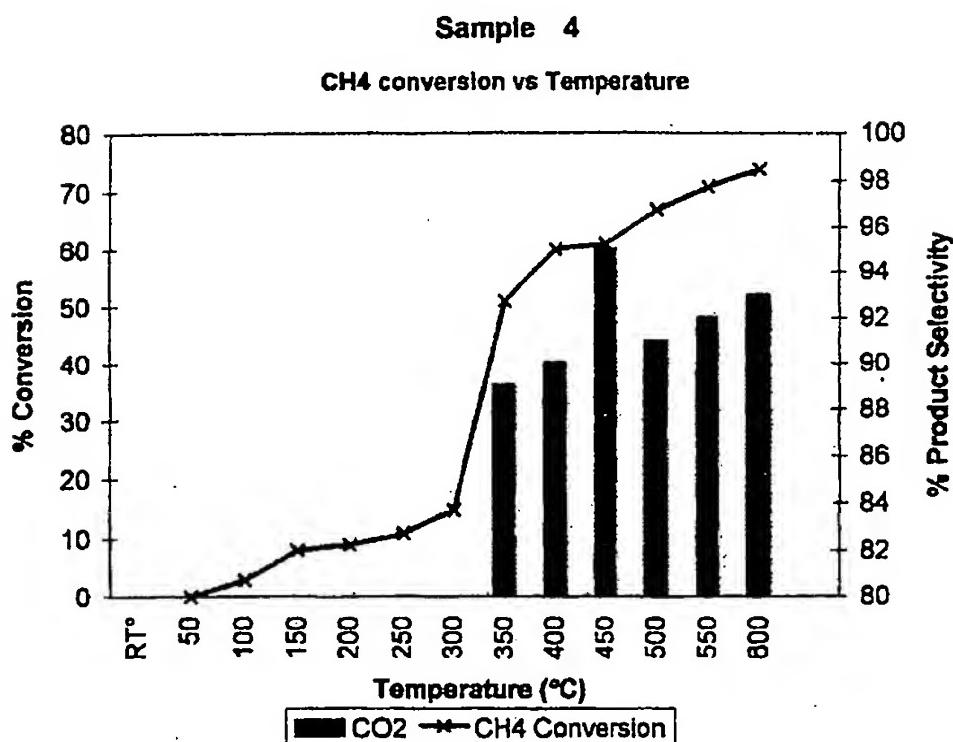
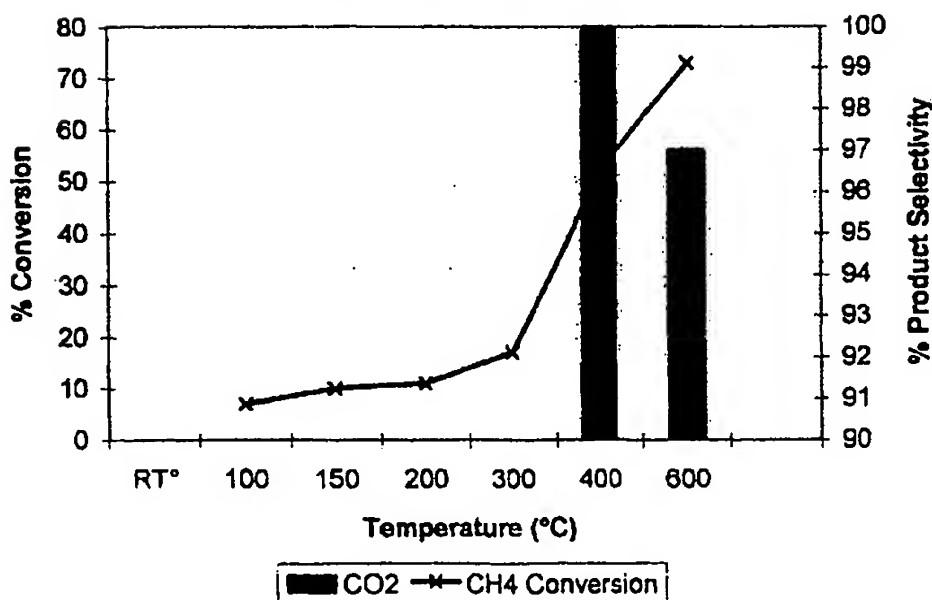
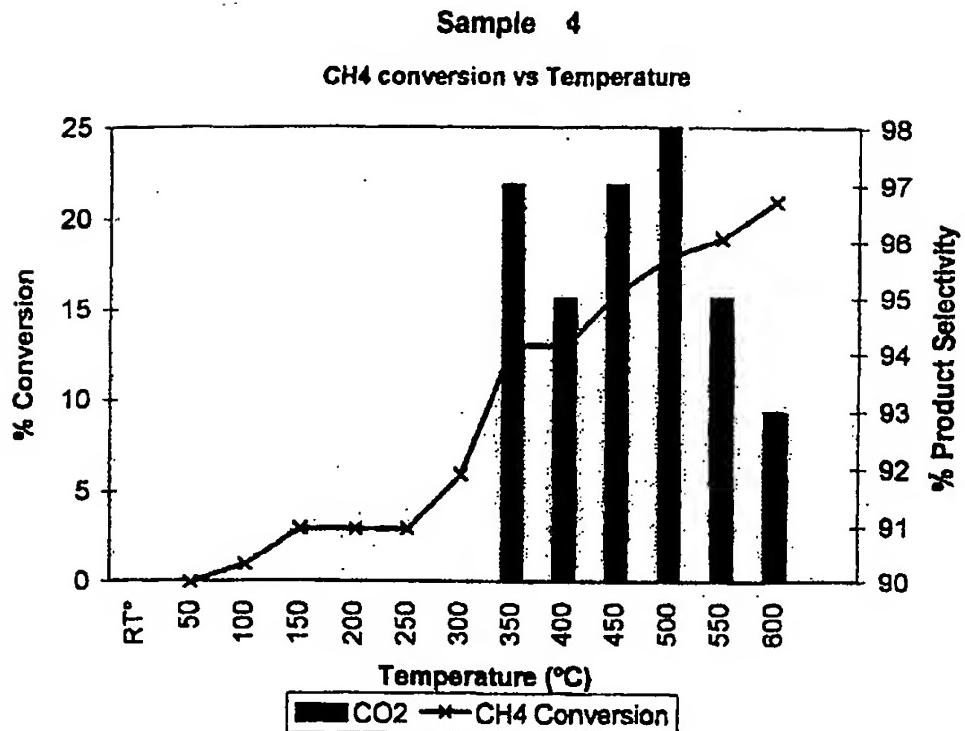
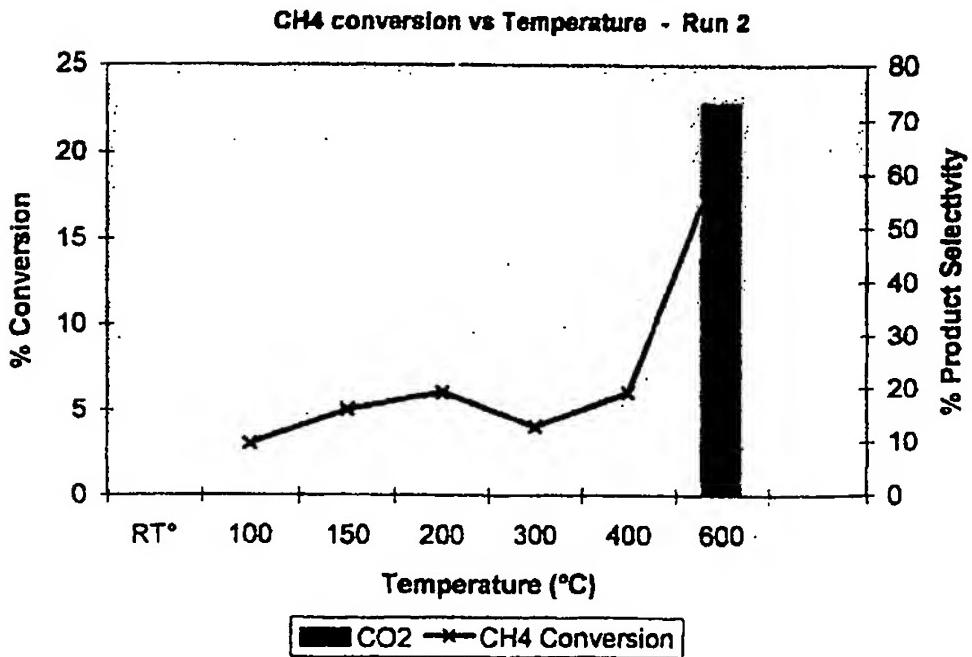
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Figure 3:Partial Methane Oxidation (25% CH₄, 15.8% O₂)**Repeat Test (25% CH₄, 15.8% O₂)****Sample 4****CH₄ conversion vs Temperature - Run 2**

Figure 4:
Partial Methane Oxidation (25% CH₄, 3.9% O₂)



Repeat Test (25% CH₄, 3.8% O₂)
Sample 4



INTERNATIONAL SEARCH REPORT

I National Application No
PCT/BG 98/00016

A. CLASSIFICATION OF SUBJECT MATTER		H01M8/12	H01M4/92	H01M4/90	
IPC 6	B01J23/52	B01J23/63			
H01M8/06					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols)					
IPC 6 B01J H01M					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category *	Citation of document, with indication, where appropriate, of the relevant passages			Relevant to claim No.	
E,L	WO 98 51401 A (LAMAN CONSULTANCY LIMITED ;PETROV LACHEZAR ANGELOV (BG)) 19 November 1998 "L" so quoted for its casting doubt on the validity of the priority claims see page 3, paragraph 2 see page 3, paragraph 4 see page 4, line 2 - line 4 see claims 1-3,5-8 see examples 1,5 ---			1-4,6	
X	WO 96 14153 A (GRIGOROVA BOJIDARA ;PALAZOV ATANAS (ZA); MELLOR JOHN (ZA); TUMILTY) 17 May 1996 see page 2, line 16 - page 3, line 13 see page 4, line 22 - line 25 see tables 1,2 see claims 1-5,7,9,10 ---			6	
A	WO 96 14153 A (GRIGOROVA BOJIDARA ;PALAZOV ATANAS (ZA); MELLOR JOHN (ZA); TUMILTY) 17 May 1996 see page 2, line 16 - page 3, line 13 see page 4, line 22 - line 25 see tables 1,2 see claims 1-5,7,9,10 ---			1,2,4	
<i>mention of fuel cell electrode</i>				-/-	
<input checked="" type="checkbox"/>	Further documents are listed in the continuation of box C.			<input checked="" type="checkbox"/>	Patent family members are listed in annex.
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed					"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
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INTERNATIONAL SEARCH REPORT

I	nternational Application No PCT/BG 98/00016
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 19843 A (ANGLO AMERICAN RES LAB PTY LTD ;TUMILTY JAMES ANTHONY JUDE (ZA)) 27 July 1995 see page 4, paragraph 2 see page 5, paragraph 5 - page 6, paragraph 2 see page 6, paragraph 4 - page 7, paragraph 1 see claims 19-21 ---	6
A	see page 4, paragraph 2 see page 5, paragraph 5 - page 6, paragraph 2 see page 6, paragraph 4 - page 7, paragraph 1 see claims 19-21 ---	1,2,4
X	M. HARUTA, A.UEDA, S. TSUBOTA, R. M. TORRES SANCHEZ: "Low-temperature catalytic combustion of methanol and its decomposed derivatives over supported gold catalysts" CATALYSIS TODAY, vol. 29, 1996, pages 443-447, XP002092222 see page 443, left-hand column, paragraph 1 see page 444, left-hand column, paragraph 4 see page 445, left-hand column, paragraph 1 see page 446, right-hand column, paragraph 2 ---	6,9
A	see page 444, left-hand column, paragraph 4 see page 445, left-hand column, paragraph 1 see page 446, right-hand column, paragraph 2 ---	1,2
X	CHEMICAL ABSTRACTS, vol. 127, no. 5, 4 August 1997 Columbus, Ohio, US; abstract no. 68522, NAGANO, SHIN ET AL: "Low temperature polymer electrolyte fuel cells" XP002092522 see abstract -& PATENT ABSTRACTS OF JAPAN vol. 097, no. 009, 30 September 1997 & JP 09 129243 A (TOYOTA CENTRAL RES & DEV LAB INC), 16 May 1997 see abstract & JP 09 129243 A (TOYOTA CENTRAL RESEARCH AND DEVELOPMENT LABORATORIES, INC., JAPAN) ---	6,9
A	see abstract -& PATENT ABSTRACTS OF JAPAN vol. 097, no. 009, 30 September 1997 & JP 09 129243 A (TOYOTA CENTRAL RES & DEV LAB INC), 16 May 1997 see abstract & JP 09 129243 A (TOYOTA CENTRAL RESEARCH AND DEVELOPMENT LABORATORIES, INC., JAPAN) ---	1,2,4
X	US 4 839 327 A (HARUTA MASATAKE ET AL) 13 June 1989 see column 2, line 11 - line 15 see column 3, line 12 - line 40 see column 4, line 11 - line 17 see column 7, line 41 - line 44 see example 1 ---	6,8,9
A	see column 2, line 11 - line 15 see column 3, line 12 - line 40 see column 4, line 11 - line 17 see column 7, line 41 - line 44 see example 1 ---	1,2,4
X	EP 0 351 123 A (JOHNSON MATTHEY PLC) 17 January 1990 see page 2, line 1 - line 6 see page 2, line 30 - line 43 see claims 1,2,4 ---	6,7
A	see page 2, line 1 - line 6 see page 2, line 30 - line 43 see claims 1,2,4 ---	1,4

INTERNATIONAL SEARCH REPORT

I	national Application No
PCT/BG 98/00016	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 416 710 A (VEG GASINSTITUUT NV) 13 March 1991 see page 7, line 13 - line 29 ---	6,7
X	EP 0 602 865 A (JOHNSON MATTHEY PLC) 22 June 1994	6
A	see page 3, line 5 - line 12 see page 3, line 21 - line 27 see examples 3,8 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 004, 31 May 1995 & JP 07 008797 A (AGENCY OF IND SCIENCE & TECHNOL), 13 January 1995 see abstract ---	1,4
A	WO 96 32188 A (GASTEC NV ;WAL WILLEM JOHAN JACOB V D (NL); WINGERDEN ANTONIUS JOH) 17 October 1996 see page 9, line 8 - line 14 see page 18, line 3 - line 19 see example 1 -----	6,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No

PCT/BG 98/00016

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9851401	A 19-11-1998	NONE		
WO 9614153	A 17-05-1996	AU 698375 B AU 3809995 A CN 1171063 A EP 0789621 A JP 10509377 T ZA 9509075 A		29-10-1998 31-05-1996 21-01-1998 20-08-1997 14-09-1998 22-05-1996
WO 9519843	A 27-07-1995	AU 690956 B AU 1461595 A CA 2182003 A EP 0741607 A IL 112414 A JP 9508058 T US 5665668 A ZA 9500584 A		07-05-1998 08-08-1995 27-07-1995 13-11-1996 16-08-1998 19-08-1997 09-09-1997 04-10-1995
US 4839327	A 13-06-1989	JP 1828306 C JP 5034284 B JP 63252908 A		15-03-1994 21-05-1993 20-10-1988
EP 0351123	A 17-01-1990	DE 68908639 D DE 68908639 T ES 2043021 T JP 2103867 A US 5246791 A		30-09-1993 13-01-1994 16-12-1993 16-04-1990 21-09-1993
EP 0416710	A 13-03-1991	NL 8902250 A AT 111767 T AU 628636 B AU 6200290 A CA 2024524 A DE 69012721 D DE 69012721 T DK 416710 T ES 2064602 T JP 3165831 A RU 2013118 C US 5366719 A		02-04-1991 15-10-1994 17-09-1992 14-03-1991 09-03-1991 27-10-1994 19-01-1995 27-03-1995 01-02-1995 17-07-1991 30-05-1994 22-11-1994
EP 0602865	A 22-06-1994	AU 675463 B AU 5247493 A CA 2111529 A JP 6219721 A US 5480854 A		06-02-1997 30-06-1994 19-06-1994 09-08-1994 02-01-1996
WO 9632188	A 17-10-1996	NL 1000146 C AU 5164196 A EP 0869842 A		15-10-1996 30-10-1996 14-10-1998